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(71) Applicant (*for all designated States except US*): **BLUESCOPE STEEL LIMITED** [AU/AU]; Level 11, 120 Collins Street, Melbourne, Victoria 3000 (AU).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **RENSHAW, Wayne** [AU/AU]; 29 Coachwood Drive, Unanderra, New South Wales 2526 (AU). **LIU, Qiyang** [AU/AU]; 12 Welmont Place, Mount Keira, New South Wales 2500 (AU).

(74) Agent: **GRIFFITH HACK**; 509 St Kilda Road, Melbourne, Victoria 3004 (AU).

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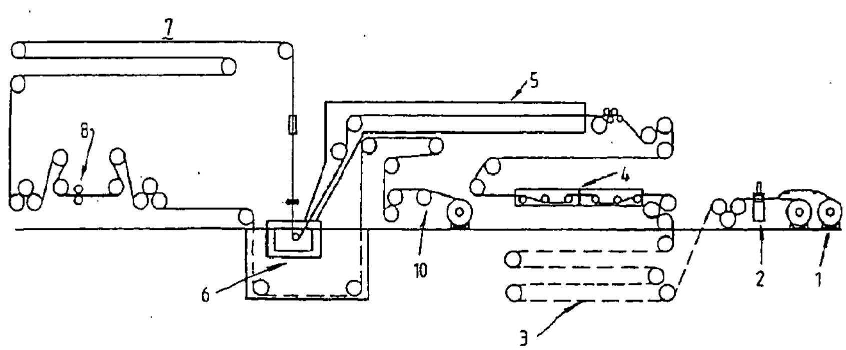
(54) Title: A METHOD OF CONTROLLING SURFACE DEFECTS IN METAL-COATED STRIP



(57) **Abstract:** A method of controlling "rough coating" and "pinhole - uncoated" surface defects on a steel strip coated with a aluminium-zinc-silicon alloy. The alloy has 50-60 %wt Al, 37-46 %wt Zn and 1.2-2.3 %wt Si. The method includes heat treating the steel strip in a heat treatment furnace (5) and thereafter hot-dip coating the strip in a molten bath (6) and thereby forming a coating of the alloy on the steel strip. The method is characterised by controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be at least 2ppm.

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A METHOD OF CONTROLLING SURFACE DEFECTS IN METAL-COATED STRIP

The present invention relates to controlling surface defects, as described hereinafter, in steel strip that has a corrosion-resistant metal coating that is formed on the strip by hot-dip coating the strip in a molten bath of coating metal.

The present invention relates particularly but not exclusively to metal coated steel strip that can be cold formed (e.g. by roll forming) into an end-use product, such as roofing products.

The present invention relates particularly but not exclusively to metal coated steel strip having an aluminium-zinc-silicon alloy coating that can be cold formed (e.g. by roll forming) into an end-use product, such as roofing products. The applicant is interested particularly in aluminium-zinc-silicon alloy coated steel strip that is sold in Australia under the Registered trade mark ZINCALUME and in other countries under the Registered trade mark GALVALUME.

The present invention also relates particularly but not exclusively to metal coated steel strip having an aluminium-zinc-silicon alloy coating with small sponge size, i.e. a coating with an average spangle size of the order of less than 0.5mm. Coated steel strip products with larger spangle size do not tend to show the generally small defects because the defects are camouflaged by the appearance of the spangle pattern.

The term "aluminium-zinc-silicon alloy" is understood herein to mean alloys comprising the following ranges in weight percent of the elements aluminium, zinc and silicon:

Aluminium:	50-60
Zinc:	37-46
Silicon:	1.2-2.3

The term "aluminium-zinc-silicon" alloy is also understood herein to mean alloys that may or may not contain other elements, such as, by way of example, any one or more of iron, vanadium, chromium, and magnesium.

In the conventional hot-dip metal coating method, steel strip generally passes through one or more heat treatment furnaces and thereafter into and through a bath of molten coating metal, such as aluminium-zinc-silicon alloy, held in a coating pot. The furnaces may be arranged so that the strip travels horizontally through the furnaces. The furnaces may also be arranged so that the strip travels vertically through the furnaces and passes around a series of upper and lower guide rollers. The coating metal is usually maintained molten in the coating pot by the use of heating inductors. The strip usually exits the heat treatment furnaces via an outlet end section in the form of an elongated furnace exit chute or snout that dips into the bath. Within the bath the strip passes around one or more sink rolls and is taken upwardly out of the bath. After leaving the coating bath the strip passes through a coating thickness control station, such as a gas knife or gas wiping station, at which its coated surfaces are subjected to jets of wiping gas to control the thickness of the coating. The coated strip then passes through a cooling section and is subjected to forced cooling. The cooled strip may thereafter be optionally conditioned by passing the coated strip successively through a skin pass rolling section (also known as a temper rolling section) and a tension levelling section. The conditioned strip is coiled at a coiling station.

The present invention is concerned particularly but not exclusively with minimising the presence of particular surface defects on steel strip that has been hot dip coated with an aluminium-zinc-silicon alloy.

The particular surface defects are described by the applicant as "rough coating" and "pinhole - uncoated" defects. Typically, a "rough coating" defect is a region that has a substantial variation in coating over a 1mm length of strip, with the thickness varying between 10 micron thick and 40 micron thick. Typically, a "pinhole - uncoated" defect is a very small region (<0.5mm in diameter) that is uncoated.

In general terms, the present invention provides a method of controlling surface defects of the type described above on a steel strip coated with an aluminium-zinc-silicon alloy which includes the steps of: successively passing the steel strip through a heat treatment furnace and a bath of molten aluminium-zinc-silicon alloy, and:

(a) heat treating the steel strip in the heat treatment furnace; and

(b) hot-dip coating the strip in the molten bath and thereby forming a coating of the alloy on the steel strip; and

which method is characterised by controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be at least 2ppm.

The invention is based on the results of work carried out by the applicant that established that strontium and calcium, separately and in combination,

substantially reduce the number of the above-described surface defects that form on steel strip that is hot dip coated in a molten bath of aluminium-zinc-silicon alloy.

The applicant has observed that "rough coating" and "pinhole - uncoated" surface defects are always associated with small areas where the metal coating has not alloyed with the steel strip.

Whilst not wishing to be bound by the following comments, the applicant believes that oxides on the surface of the strip may be one factor that causes the absence of alloying of the aluminium-zinc-silicon alloy coating and the steel strip in the small areas. The applicant also believes that one major source of the oxides is the surface of the molten bath. The surface oxides are solid oxides that are formed from metals in the molten bath as a result of reactions between molten bath metal and water vapour in the snout above the molten bath. In a molten bath of an aluminium-zinc-silicon alloy, in addition to aluminium, zinc, and silicon, the molten bath contains minor amounts of other metals including magnesium. The applicant believes that surface oxides are taken up by strip as the strip passes through the oxide layer in order to enter the molten bath. The applicant has established that strontium and calcium minimise the amount of oxides that form on the bath surface and suspects that these elements may reduce the amount of oxides that are available to be taken up by the strip. The applicant also suspects that, alternatively or in combination, strontium and calcium may modify the properties of the surface oxides and, for example, increase the strength of the oxides whereby there is less likelihood that oxides will break away from the bath surface and be taken up by strip.

The above-described method is characterised by the deliberate inclusion of the elements strontium and/or

calcium in the coating aluminium-zinc-silicon alloy. In the context of the present invention, the elements are regarded as beneficial.

The aluminium-zinc-silicon alloy may include other elements.

However, preferably the aluminium-zinc-silicon alloy does not contain the elements vanadium and/or chromium as deliberate alloy elements - as opposed to being present in trace amounts for example due to contamination in the molten bath.

In a situation in which the molten bath contains strontium and no calcium, preferably the method includes controlling the concentration of strontium in the molten bath to be in the range of 2-4ppm.

More preferably the strontium concentration is 3ppm.

In a situation in which the molten bath contains calcium and no strontium, preferably the method includes controlling the concentration of calcium in the molten bath to be in the range of 4-8ppm.

More preferably the calcium concentration is 6ppm.

In a situation in which the molten bath contains strontium and calcium, preferably the method includes controlling the concentration of strontium and calcium in the molten bath to be at least 4ppm.

Preferably the method includes controlling the concentration of strontium and calcium in the molten bath to be in the range of 2-12ppm.

Preferably the method includes controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be at no more than 150ppm.

More preferably method includes controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be no more than 50ppm.

The applicant has found that the control of strontium and calcium concentrations in the molten bath has a particularly beneficial effect on aluminium-zinc-silicon alloys that contain magnesium.

Preferably aluminium-zinc-silicon alloys have a magnesium concentration of less than 1%.

More preferably aluminium-zinc-silicon alloys have a magnesium concentration of less than 50ppm.

The concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath may be controlled by any suitable means.

One option, which is preferred by the applicant, is to specify a minimum concentration(s) of strontium and/or calcium in the aluminium that is supplied to form the aluminium-zinc-silicon alloy for the molten bath.

Another, although not the only other, option is to periodically dose the molten bath with amounts of strontium and/or calcium that are required to maintain the concentration(s) at a required concentration.

The present invention is particularly advantageous for "minimum spangle" strip.

The term "minimum spangle" strip is understood herein to mean metal coated strip that has spangles that are less than 0.5mm, preferably less than 0.2mm, in the major dimension of the spangles substantially across the surface of the strip.

Standard spangled strip obscures the surface defects. Minimum spangle strip does not obscure the surface defects.

Minimum spangle strip may be formed by any suitable method steps, such as described in International application PCT/US00/23164 (WO 01/27343) in the name of Bethlehem Steel Corporation. The disclosure in the specification of the International application is incorporated herein by cross-reference.

The present invention is also particularly advantageous for steel strip that does not have a surface appearance, such as spangled strip, that obscures the surface defects and has not been conditioned by heavily skin pass rolling the strip to obscure the surface defects. An example of such a non-heavy skin passed rolled strip is steel strip that is conditioned to have a residual stress of no more than 100 MPa in the strip - as described by way of example in Australian complete application 43836/01 in the name of the applicant. The disclosure in the Australian complete application is incorporated herein by cross-reference.

The furnace may be any suitable furnace, such as a horizontal furnace or a vertical furnace.

Preferably the furnace has an elongated furnace

exit chute or snout that extends into the bath.

According to the present invention there is also provided a steel strip coated with an aluminium-zinc-silicon alloy produced by the above-described method.

The present invention is described further by way of example with reference to the accompanying drawings of which:

Figure 1 is a schematic drawing of one embodiment of a continuous production line for producing steel strip coated with aluminium-zinc-silicon alloy in accordance with the method of the present invention

Figure 2 a graph of the estimated concentration of strontium over a 5 month time period in a molten bath containing an aluminium-zinc-silicon alloy that forms part of a steel strip coating line of the applicant at a plant of the applicant at Westernport, Victoria; and

Figure 3 is a graph of the frequency of the above-described surface defects in the aluminium-zinc-silicon alloy coatings formed by hot dip coating steel strip through the molten bath during part of the time period covered by the Figure 2 graph.

With reference to Figure 1, in use, coils of cold rolled steel strip are uncoiled at an uncoiling station 1 and successive uncoiled lengths of strip are welded end to end by a welder 2 and form a continuous length of strip.

The strip is then passed successively through an accumulator 3, a strip cleaning section 4 and a furnace assembly 5. The furnace assembly 5 includes a preheater, a preheat reducing furnace, and a reducing furnace.

The strip is heat treated in the furnace assembly 5 by careful control of process variables including:(i) the temperature profile in the furnaces, (ii) the reducing gas concentration in the furnaces, (iii) the gas flow rate through the furnaces, and (iv) strip residence time in the furnaces (ie line speed).

The process variables in the furnace assembly 5 are controlled so that there is removal of iron oxide residues from the surface of the strip and removal of residual oils and iron fines from the surface of the strip.

The heat treated strip is then passed via an outlet snout downwardly into and through a molten bath containing an aluminium-zinc-silicon alloy held in a coating pot 6 and is coated with aluminium-zinc-silicon alloy. Preferably the aluminium-zinc-silicon alloy contains the elements strontium and/or calcium. Preferably the aluminium-zinc-silicon alloy does not contain the elements vanadium and/or chromium. The aluminium-zinc-silicon alloy is maintained molten in the coating pot by use of heating inductors (not shown). Within the bath the strip passes around a sink roll and is taken upwardly out of the bath. Both surfaces of the strip are coated with the aluminium-zinc-silicon alloy as it passes through the bath.

After leaving the coating bath 6 the strip passes vertically through a gas wiping station (not shown) at which its coated surfaces are subjected to jets of wiping gas to control the thickness of the coating.

The coated strip is then passed through a cooling section 7 and subjected to forced cooling.

The cooled, coated strip, which typically is minimum spangle strip, is then passed through a rolling

section 8 that conditions the surface of the coated strip.

The coated strip is thereafter coiled at a coiling station 10.

The above-described method is characterised by controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the aluminium-zinc-silicon alloy in the bath to be at least 2ppm, more preferably at least 3ppm, and preferably less than 150ppm and more preferably less than 50ppm.

As is indicated above, the applicant established the importance of strontium and calcium in the course of work carried out by the applicant.

The work was carried out as part of an investigation by the applicant to identify the cause of an unexpected substantial increase in the number of the above-described defects during a production phase on the aluminium-zinc-silicon alloy coating lines at the Westernport plant of the applicant. The coating lines were producing steel strip having a standard spangle coating.

The investigation was wide ranging and extensive and considered a significant number of possible causes of the surface defects before any consideration was given to the bath composition being the cause of the surface defects.

Unexpectedly, the applicant identified an absence of strontium in the molten baths in the coating lines as the cause of the sudden increase in the number of surface defects on the steel strip.

The applicant found that the onset of the substantial increase in the surface defects corresponded

well with a change in the composition of the molten baths in the coating lines. The company supplying the aluminium ingots used as feed material to make the molten aluminium-zinc-silicon alloy for the baths had made a change to the manufacturing process for the aluminium ingots. Prior to the change, the aluminium supplied by the company included small amounts of strontium as a contaminant that resulted in bath concentrations of strontium estimated to be in the range of 10-18ppm. The change removed strontium altogether from the aluminium.

With reference to Figure 2, the change in the aluminium ingot feed for the molten metal for one of the lines occurred around 18 April 1995. This aluminium ingot feed was maintained until early July. The applicant found that there was a substantial increase in the number of surface defects in metal coated coils produced after 18 April. In order to establish the impact of bath strontium on the numbers of surface defects, the applicant decided to re-introduce strontium to the molten bath via the addition of aluminium-10% strontium "piglets". The piglets were added to the molten bath in early July. The strontium had a dramatic impact on the number of surface defects. With reference to Figure 3, the arrow marked "Sr Added" indicates the dividing line between coated steel coils produced prior and after the addition of the piglets. It is evident from Figure 3 that there was a substantially lower number of surface defects in the coated coils produced after the addition of the piglets. Further work carried out by the applicant indicates that the bath concentration of strontium should be controlled to be at least 2ppm and more preferably at least 3ppm.

Many modifications may be made to the preferred embodiment described above without departing from the spirit and scope of the present invention.

CLAIMS

1. A method of controlling surface defects of the type described herein on a steel strip coated with a aluminium-zinc-silicon alloy which includes the steps of: successively passing the steel strip through a heat treatment furnace and a bath of molten aluminium-zinc-silicon alloy, and:

(a) heat treating the steel strip in the heat treatment furnace; and

(b) hot-dip coating the strip in the molten bath and thereby forming a coating of the alloy on the steel strip; and

which method is characterised by controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be at least 2ppm.

2. The method defined in claim 1 wherein, in a situation in which the bath contains strontium and no calcium, the method includes controlling the concentration of strontium in the molten bath to be in the range of 2-4ppm.

3. The method defined in claim 2 wherein the concentration of strontium is 3ppm in the molten bath.

4. The method defined in claim 1,wherein in a situation in which the molten bath contains calcium and not strontium, the method includes controlling the concentration of calcium in the molten bath to be in the range of 4-8ppm.

5. The method defined in claim 4 wherein the

concentration of calcium is 6ppm.

6. The method defined in any one of the preceding claims includes controlling the concentration of strontium and calcium in the molten bath to be in the range of 2-12ppm.

7. The method defined in any one of the preceding claims includes controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be no more than 50ppm.

8. The method defined in any one of the preceding claims wherein the aluminium-zinc-silicon alloy does not contain the elements vanadium and/or chromium as deliberate alloy elements.

9. The method defined in any one of the preceding claims wherein the aluminium-zinc-silicon alloy contains magnesium.

10. The method defined in claim 7 wherein the aluminium-zinc-silicon alloy has a magnesium concentration of less than 1%.

11. The method defined in any one of the preceding claims includes controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath by specifying a minimum concentration(s) of strontium and/or calcium in the aluminium that is supplied to form the aluminium-zinc-silicon alloy for the molten bath.

12. The method defined in any one of claims 1 to 8 includes controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath by periodically dosing the molten bath with amounts of

strontium and/or calcium that are required to maintain the concentration(s) at a required concentration.

13. The method defined in any one of the preceding claims wherein the aluminium-zinc-silicon alloy steel strip is minimum spangle strip.

14. A method of controlling surface defects of the type described herein on a steel strip having a minimum spangle coating of an aluminium-zinc-silicon alloy which includes the steps of: successively passing the steel strip through a heat treatment furnace and a bath of molten aluminium-zinc-silicon alloy, and:

(a) heat treating the steel strip in the heat treatment furnace; and

(b) hot-dip coating the strip in the molten bath and thereby forming a coating of the alloy on the steel strip; and

which method is characterised by controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be at least 2ppm.

15. A method of controlling surface defects of the type described herein on a steel strip coated with an aluminium-zinc-silicon alloy, which aluminium-zinc-silicon alloy contains the elements strontium and/or calcium and does not contain the elements vanadium and/or chromium, which method includes the steps of: successively passing the steel strip through a heat treatment furnace and a bath of molten aluminium-zinc-silicon alloy, and:

(a) heat treating the steel strip in the heat treatment furnace; and

(b) hot-dip coating the strip in the molten bath and thereby forming a coating of the alloy on the steel strip; and

which method is characterised by controlling the concentration of (i) strontium or (ii) calcium or (iii) strontium and calcium in the molten bath to be at least 2ppm.

16. A metal coated steel strip produced by the method defined in any one of the preceding claims.

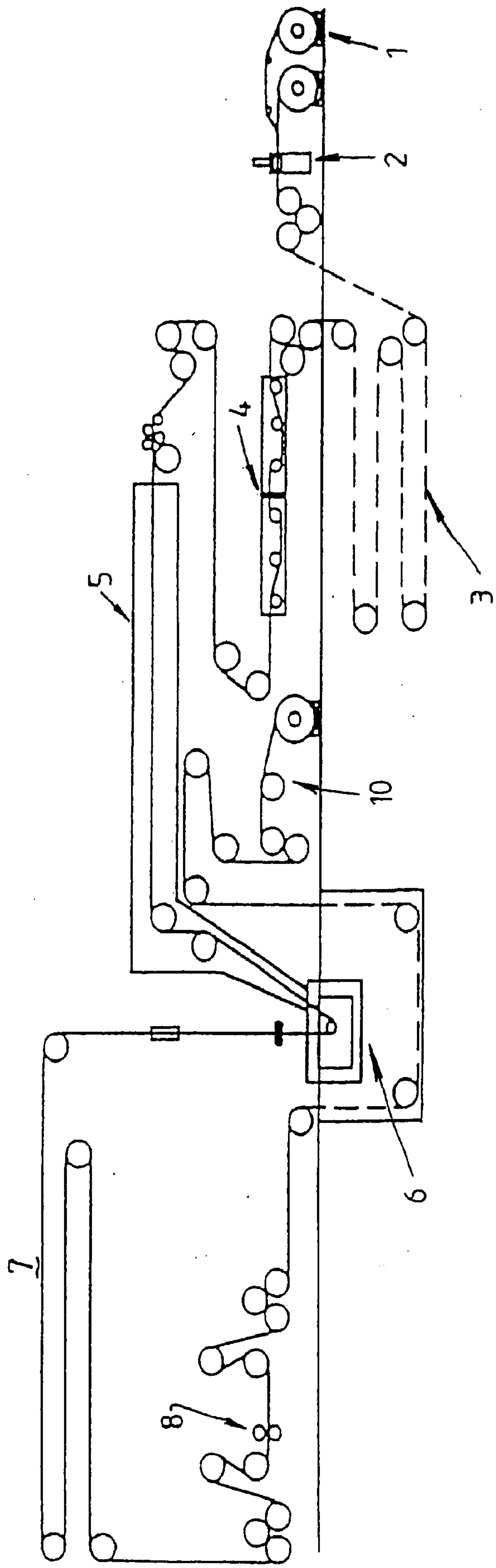
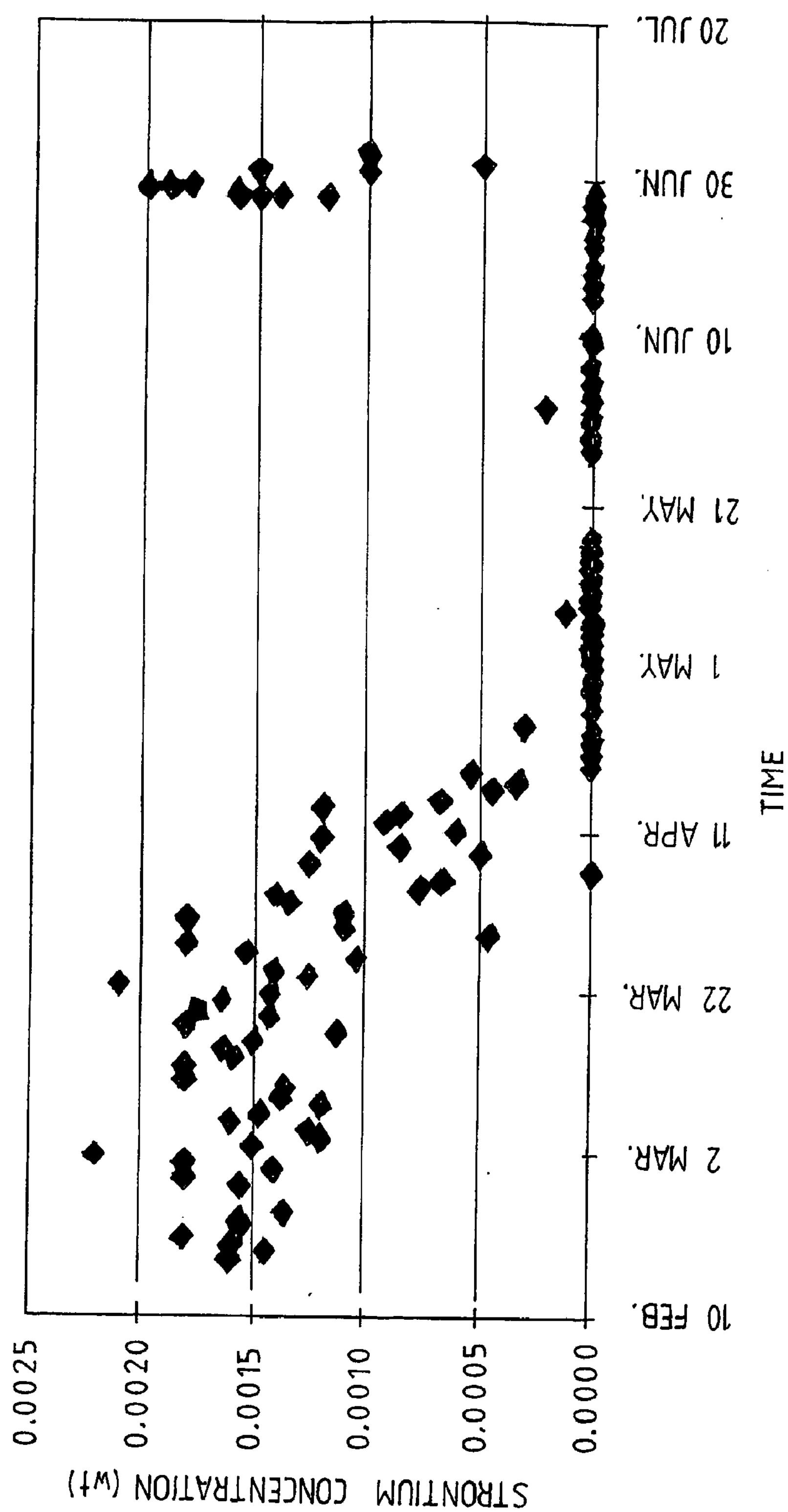


FIG. 1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1 MAY.
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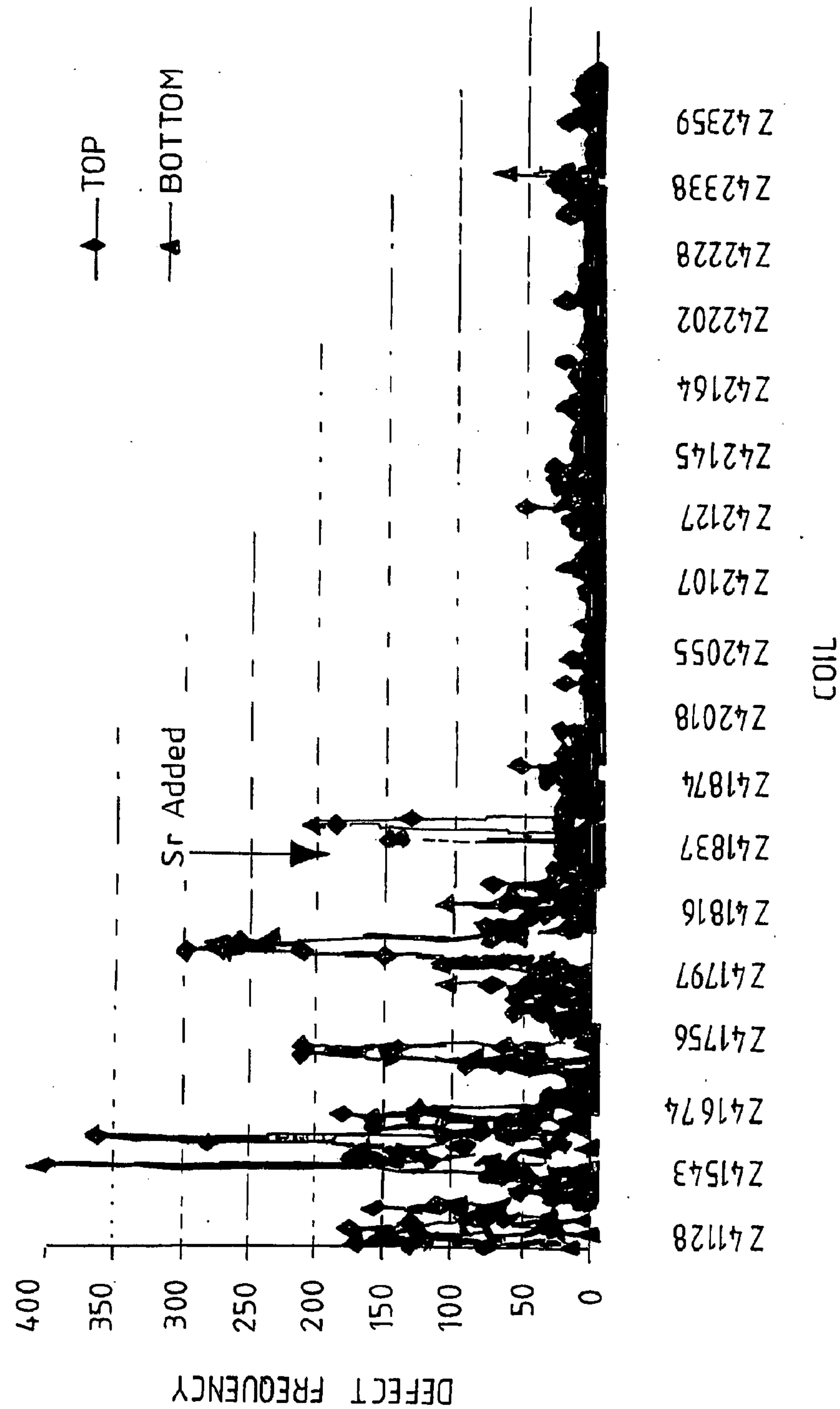
30 JUN.
20 JUL.

FIG. 2.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Z42164
Z42202
Z42228
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Z 42359

FIG. 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/000345

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: C23C 2/12, 2/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI: (C23C 1/- or 2/-) and (Strontium or Sr or Calcium or Ca)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 2002-753641/82, Class M13, JP 2002-241917 A (SUMITOMO METAL IND LTD) 28 August 2002 See Abstract	1-8, 10-16
X	US 5217759 A (LAMBERIGTS et al) 8 June 1993 See Abstract, column 1 lines 34-55, column 2 line 35-38	1-3, 6-7, 10-14, 16
A	US 4456663 A (LEONARD) 26 June 1984 See Abstract	1-16

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

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Date of the actual completion of the international search	Date of mailing of the international search report
3 May 2004	6 MAY 2004

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. (02) 6285 3929

Authorized officer

ROGER HOWE
Telephone No : (02) 6283 2159

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/000345

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
JP	2002241917						
US	5217759	AT	75191	AU	75024/91	BE	1004077
		BE	1004839	CA	2040376	CS	9101006
		DE	4111410	ES	2038885	FI	911773
		FR	2660937	GB	2243843	JP	6340957
		LU	87916	NL	9100638	SE	9101053
		US	5279903				
US	4456663	AU	91047/82	BR	8206921	EP	0080903
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